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14. ABSTRACT
This grant funded the acquisition of a computer laboratory for multiscale modeling of nanomaterials. The laboratory includes a share in new Rutgers School of Engineering computational facilities and several PC workstation furnished with commercial and in-house simulation software. This equipment supports the computational needs of the group of the PI at Rutgers University. The group continues the research on novel polymeric materials needed for chemical and biological defense.

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Report Title

Final Report: Computer laboratory for multi-scale simulations of novel nanomaterials

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This grant funded the acquisition of a computer laboratory for multiscale modeling of nanomaterials. The laboratory includes a share in new Rutgers School of Engineering computational facilities and several PC workstation furnished with commercial and in-house simulation software. This equipment supports the computational needs of the group of the PI at Rutgers University. The group continues the research on novel polymeric materials needed for chemical and biological defense.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

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(b) Papers published in non-peer-reviewed journals (N/A for none)

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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

Technology Transfer

FINAL REPORT: W911 NF-12-1-0328

"Computer laboratory for multi-scale simulations of novel nanomaterials"

PI: Alexander V. Neimark,
Co-PI: Aleksey Vishnyakov
Department of Chemical and Biochemical Engineering,
Rutgers the State University of New Jersey

Grant period: July 1 2012 to July 1 2014

PROJECT SUMMARY

This grant funded the acquisition of a computer laboratory for multiscale modeling of nanomaterials. The laboratory includes a share in new Rutgers School of Engineering computational facilities and several PC workstation furnished with commercial and in-house simulation software. This equipment supports the computational needs of the group of the PI at Rutgers University. The group continues the research on novel polymeric materials needed for chemical and biological defense, which is performed in collaboration with Dr Walter Zukas from Natick RDEC (Natick, MA). It was supported by DTRA (grant HDTRA1-08-1-0042) and is currently supported by DTRA grant "Mass Transport, Kinetics, and Catalytic Activities of Multicatalyst Polyelectrolyte Membranes" (HDTRA1-14-1-0015)

The research performed by Neimark's group aims at (1) fundamental understanding of interactions of permselective self-decontaminating polyelectrolyte membranes (PEM) with chemical warfare agents (CWA) and their simulants and (2) development of new simulation methods and computational schemes for multiscale modeling of polymers. Permselective ion-exchange membranes for protective clothing, fuel cells, and batteries are of special interest to US Army. These materials include Nafion-type polymers, sulfonated block-copolymers, ionic Kevlar, novel polymers produced with ionic liquids, etc. Inclusion of catalytic nanoparticles into permselective polyelectrolytes opens perspectives for synthesis of self-decontaminating protective membranes that not only block the toxic agents, but also promote their destruction via catalytic oxidation and hydrolysis. These multicatalyst nanocomposite membranes have a potential to become versatile platforms for various applications, including catalytic photosynthetic systems and sensors.

Engineering properties of polyelectrolyte-nanoparticle composites are determined by the their nanostructure. Upon hydration, polyelectrolyte segregates into hydrophilic and hydrophobic domains. Segregation morphology determines sorption and transport of chemical agents. Catalytic properties crucially depend on nanoparticle distribution in the polyelectrolyte matrix and the molecular structure of particle/polymer interface. Molecular design of these systems involves the whole suite of molecular simulation tools starting from ab-initio and atomistic level simulations to coarse-grained mesoscopic methods to macroscopic multiphase modeling. This modeling is computationally expensive and requires calculations on fast, parallel platforms with rapid turnaround and efficient optimization algorithms. The equipment purchased with W911 NF-12-1-0328 grant is essential for success of our research program. The equipment and software also plays important role in the new Rutgers

School of Engineering course "Fundamentals of Nanoscale Thermodynamics and Transport" developed and taught by Neimark and Vishnyakov.

Full reporting on the research accomplishments achieved using the equipment acquired with the DURIP funds may be found in research papers and technical reports on DTRA projects DTRA HDTRA1-08-1-0042 and HDTRA1-14-1-0015 available from respective journals and DTRA.

Summary Overview of the Purchase and Installation of the Equipment

Equipment or software	Vendor
256-core Linux computational cluster (2 units 256 cores each)	HP
Auxiliary hardware: network switches and cables	Netgear
Power supplies	APC
4-core workstation with GPU	Microway
Individual workstations (3)	Microway
Cloud station for large data storage	HP
3D graphics card and goggles	Nvidia
Software: PQS ab-initio licenses (cluster and workstation) Upgrade of Materials studio software suit	Parallel Quantum Solutions, Accelrys

The exact cost will be provided in the financial report generated by the business office

Major hardware: *Cluster for parallel computations* (Figure 1L) is installed at the new computational facility located at Hill Center of Rutgers University. The facility is equipped with temperature and humidity control and staffed with system administrator of high qualification and technicians. Integration of the clusters into the campus facilities made us eligible for a large (30-40%) discount from HP.

The cluster consists of two 128-core units. Each units has 8 nodes which harbor 32 4-core power efficient E5-2670 CPUs, 256 GB 4 TB of disk space. The nodes are connected via gigabit Ethernet and Infiniband cables and switches

Microway Wispering Workstations are located in the offices for the students of Neimark's group and the Department of Chemical and Biochemical Engineering. The equipment was complimented by four other PC workstations supplied by the School of Engineering. These Linux PCs are used for remote access to the cluster and the workstation equipped with Materials Studio software.

Cloud Storage station has a storage capacity of 9TB and has a capability of synchronizing selected directories with local workstations and personal notebooks of individual team members. The data is constantly accessible via Internet.

Fig 1. Left: Computational clusters from Hewlett-Packard acquired with DURP funds installed at high performance computer facilities at Rutgers Hill Center. Right: Workstations and Cloud Storage systems in students office at the Department of Chemical and Biochemical Engineering, Rutgers.

Software:

Materials Studio package from Accelrys for classical simulations of polymeric materials was upgraded and installed on a new dedicated workstation purchased with the DURIP fundes. Materials Studio software offers a wide range of capabilities:

- building molecular models of monomers and polymers,
- constructing representative models of complex amorphous systems,
- prediction of interaction parameters for liquid-liquid, polymer-polymer, and polymer-additive mixtures
- calculating the free energy of mixing of polymers and liquid crystals, adhesion strength
- classical optimization and dynamic simulations of periodic systems

Although we do not consider Materials Studio as a primary simulation tool due to the absence of code transparency, it is an incredible building and visualization tool in our research. It is especially valuable for education purposes, first of all for undergraduate student projects, for its user-friendly nature and best visualization ability. It also serves for course preparation. Although Materials studio is installed on a single PC Workstation, our server license allows a remote access to it from four different computers.

PQS ab-initio package has been upgraded and installed on a new 4-core workstation with 16Gb of RAM and 2Tb and Gforce 680 GPU for parallel computations. PQS ab-initio simulation package augmented with PQSmol visualization software is capable of

both ab-initio and classical modeling of materials. It's capabilities include geometry optimization based on restricted and open-shell Hartree-Fock, semi-empirical, or MP2 energies and gradients using various popular optimization algorithms, prediction of IR and Raman spectra, plus molecular mechanics and molecular dynamics simulations with second-generation classical forcefields and reaction path prediction. PQSmol software will also be used for visualization of simulations performed on our older cluster purchased with DoD funds in 2006-2007.

In-house software Over the years of working on various research projects funded by the DoD, we developed a number of efficient simulation codes, such as SORSIM module for simulation of sorption equilibria. Its current capabilities include simulation of sorption of complex fluids of rigid molecules in spherical, cylindrical or slit-like pores at given chemical potential in equilibrium bulk reservoir using GCMC method, obtaining equilibrium configuration of the fluid in the canonical ensemble, calculation of chemical potential using gauge cell method and calculation of density profiles. However, the code does not run in parallel environments. For mesoscale simulations, we developed a Dissipative Particle Dynamics program, which is capable of modeling fragments of segregated block copolymer membranes of several dozen of nanometers in size over microseconds using mesoscale coarse-grained models. With our own cluster for parallel simulations, we plan to build a single parallel simulation package easily extendable with addition of new modules and methods.

Summary of research accomplished using the computational laboratory

Search for novel polymeric electrolyte membranes suitable as permselective diffusion barriers is one of the key problems in engineering new protective materials for Chemical and Biological defense. These membranes must be impermeable to CWA and, at the same time, provide high water vapor permeability, small heat accumulation, and reduced weight. Our research on these materials is supported by DTRA. The goal of the project was to get a better understanding of the physical and chemical factors governing sorption and permeability of phosphoorganic agents in PEM made of sulfonated multi-block copolymers of styrene and lower olefins by means of multiscale molecular simulations. These materials are of special interest to the Army as low-cost substitutes of expensive Nafion-type membranes. To enhance experimental studies, one needs to predict how the polyelectrolyte chemistry, its composition, and counterions would affect sorption and transport of ions and chemicals in solvated membranes Concentrating on sulfonated polystyrene containing block-copolymers, we developed a hierarchical multiscale methodology for computational studies of the membrane morphology at environmental conditions, and the membrane sorption and transport properties with respect to water and nerve gases and simulants.

With molecular dynamics simulations performed on the new computational cluster, we examined the mechanisms of sorption and diffusion of sarin in hydrated polyelectrolytes. Three types of hydrated polyelectrolytes were considered – Nafion, sulfonated polystyrene (sPS) that forms the hydrophilic subphase of segregated sPS-polyolefin block copolymers, and random sPS-polyethylene copolymer. We found that sarin concentrates at the interface between the hydrophilic and hydrophobic subphases of hydrated Nafion acting as a surfactant. In hydrated sPS, where the scale of water –

polymer segregation is much smaller (1-2 nm, Figure 2), sarin also interacts favorably with hydrophobic and hydrophilic components. Water diffusion slows down as sarin content increases despite the overall increase in solvent content, which suggests that sarin and water have somewhat different pathways through the segregated membrane. Upon replacement of counterions of monovalent potassium with divalent calcium, sarin diffusion slows down, but sarin remains permeable in all ionomers considered, especially at high sarin concentrations. These properties of sarin are found to be similar to those of its common simulant dimethyl methylphosphonate.

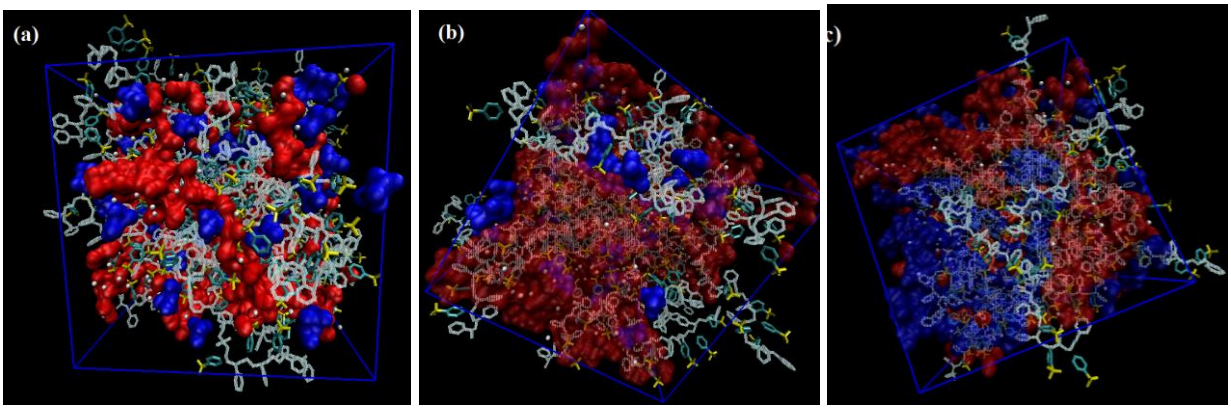

Figure 2. Snapshots of 40% sulfonated polystyrene fragments in (a) 10 wt% of sarin (solvent surface shown in red) and 10 wt% of water (solvent surface shown in blue), in (b) 10 wt% of sarin and 54 wt% of water, and in (c) 50 wt% of sarin and 50 wt% of water. Hydrophobic backbones of polymer fragments are drawn in white, and side chains are marked in green (sulfonated benzene rings) and yellow (sulfonate groups). Dots represent potassium counter ions. Box length: (a) 54.5Å, (b) 54.6Å, and (c) 54.5Å.

By means of dissipative particle dynamics (DPD) and Monte Carlo (MC) simulations, we explored geometrical, transport, and sorption properties of hydrated Nafion-type polyelectrolyte membranes. Composed of perfluorinated backbone with sulfonate sidechains, Nafion segregates into interpenetrating hydrophilic and hydrophobic subphases. This segregated morphology determines the transport properties of Nafion membranes that are widely used as compartment separators in fuel cells and other electro-chemical devices, as well as permselective diffusion barriers in protective fabrics. We introduced a coarse-grained model of Nafion, which accounts explicitly for polymer rigidity and the electrostatic interactions between anionic sidechains and hydrated metal cations. In a series of DPD simulations with increasing water content, a classical percolation transition from a system of isolated water clusters to a 3D network of hydrophilic channels was observed. The hydrophilic subphase connectivity was characterized by constructing its digitized replica and performing random walk simulations. A non-monotonic dependence of tracer diffusivity on the water content was found. This unexpected behavior was explained by formation of large and mostly isolated water domains detected at high water content and high equivalent polymer weight. Using Monte Carlo simulations, we calculated the chemical potential of water in the hydrated polymer and constructed the water sorption isotherms, which extended to the oversaturated conditions. We determined that the maximum diffusivity and the onset of formation of large water domains corresponded to the saturation conditions at

100% humidity. The oversaturated membrane morphologies generated in the canonical ensemble DPD simulations correspond to the membrane metastable and unstable states.

The molecular simulation studies were performed in concert with the experimental work at Rutgers University and Natick Soldier RDEC, Natick, MA.

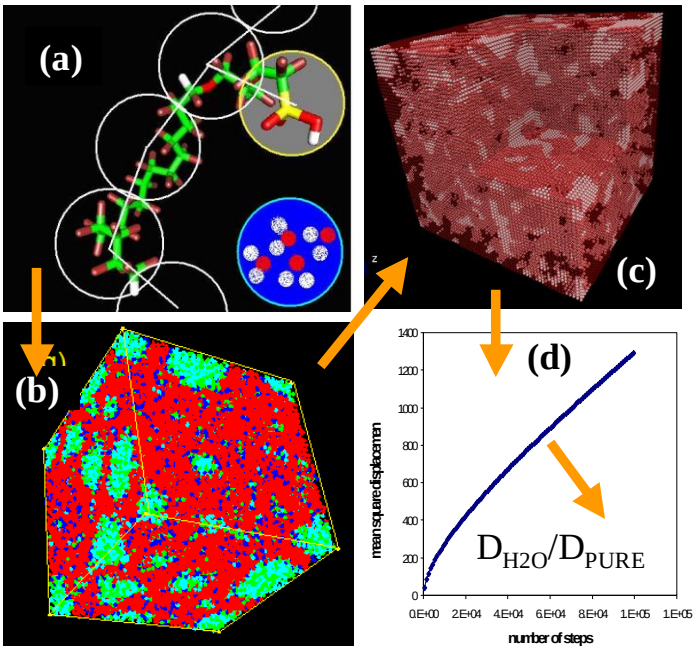

Figure 3. Approach to mesoscale simulations to water transport in hydrated Nafion polyelectrolyte. (a) mesoscale model is developed from atomistic presentation based on experimental and atomistic simulation results (b) example of hydrated Nafion structure obtained from DPD simulations (c) lattice replica of Nafion structure: each points referred to either hydrophilic or hydrophobic subphase (d) diffusion coefficient of water is obtained by random walk through the hydrophilic subphase of the lattice replica

Educational outreach

The computational laboratory serves as a primary facility for a new Rutgers School of Engineering graduate course "*Fundamentals of Nanoscale Thermodynamics and Transport*" (16:155:588) developed and introduced by Neimark and Vishnyakov in 2008. Nanoscale science and engineering operates with physical, chemical, and biological processes and objects, in which at least one dimension is smaller than micron. At the same time, the details of molecular structure and inter-molecular interactions are left to the domain of quantum mechanics. The nanoscale spans the range from ~ 1 nm (10 A) to ~1000 nm (1 mkm). The course covers the theoretical and multiscale simulation methods, which bridge macroscopic thermodynamics and continuum transport theories with atomistic quantum mechanics and molecular dynamics. The key theoretical topics include: statistical mechanics and thermodynamics of nanophases and nanostructured materials, Monte Carlo simulation of nanoscale systems, density functional theory of confined fluids, coarse-grained molecular dynamics and dissipative particle dynamics. The applications include: nanoparticles and nanocomposites, porous

materials, nanostructured colloids and surfaces, self-assembled surfactant and polymeric systems, lipid bilayers and cell membranes. The course consists of 12 theoretical lectures, 6 home works and 2 research projects. The home works and research projects form a sort of a “laboratory course”: students perform simulations of adsorption in porous materials and segregation in polymers using Monte Carlo and dissipative particle dynamics methods using our in-house software. For this purpose, they receive temporary accounts on Linux workstations of the Computational Laboratory and use them for their assignments within the course.

Publications

Lee M-T, Vishnyakov A, Gor G.Y., Neimark A.V. Interactions of Sarin with Polyelectrolyte Membranes: A Molecular Dynamics Simulation Study. J. Phys. Chem. B 117: 365-372 (2013)

Vishnyakov A., Neimark A.V. Self-assembly in Nafion membranes upon hydration: water mobility and adsorption isotherms . J. Phys. Chem. B *in press* (2014)